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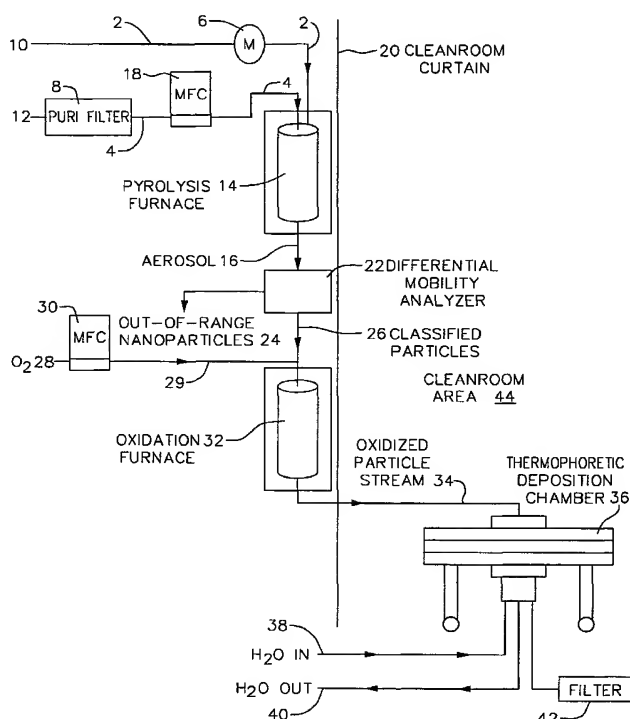
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ning of each regular issue of the PCT Gazette.

(54) Title: AEROSOL PROCESS FOR FABRICATING DISCONTINUOUS FLOATING GATE MICROELECTRONIC DEVICES



(57) Abstract: A process for forming an aerosol of semiconductor nanoparticles includes pyrolyzing a semiconductor material-containing gas then quenching the gas being pyrolyzed to control particle size and prevent uncontrolled coagulation. The aerosol is heated to densify the particles and form crystalline nanoparticles. In an exemplary embodiment, the crystalline particles are advantageously classified by size using a differential mobility analyzer and particles having diameters outside of a pre-selected range of sizes, are removed from the aerosol. In an exemplary embodiment, the crystalline, classified and densified nanoparticles are oxidized to form a continuous oxide shell over the semiconductor core of the particles. The cores include a density which approaches the bulk density of the pure material of which the cores are composed and the majority of the particle cores are single crystalline. The oxidized particles are deposited on a substrate using thermophoretic, electrophoretic, or other deposition means. The deposited particles form a stratum or discontinuous monolayer of oxidized semiconductor particles. In an exemplary embodiment, the stratum is characterized by a uniform particles density on the order of 10^{12} to 10^{13} particles/cm² and a tightly controlled range of particle sizes. A plurality of adjacent particles contact each other, but the oxide shells provide electrical isolation between the particles of the stratum. Clean processing techniques provide a density of foreign atom contamination of less than 10^{11} atoms/cm². The stratum is advantageously used as the floating gate in a non-volatile memory device

such as a MOSFET. The non-volatile memory device exhibits excellent endurance behavior and long-term non-volatility.

1 AEROSOL PROCESS FOR FABRICATING DISCONTINUOUS
 FLOATING GATE MICROELECTRONIC DEVICES

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

5 The U.S. Government has certain rights in this invention pursuant to grant DMR-9871850 awarded by the National Science Foundation.

BACKGROUND OF THE INVENTION

10 Driven by a strong demand for portable electronic devices, non-volatile memory represents an important and rapidly growing sector of today's semiconductor memory market. Polysilicon floating gate memory devices conventionally have held the largest market share of non-volatile memory devices. In today's rapidly emerging non-volatile memory device sector, non-volatile floating gate memory devices have been fabricated by embedding silicon nanoparticles within the gate oxide of metal-oxide semiconductor field effect transistors (MOSFETs). Nanoparticles are so named because they include particle diameters on the nanometer scale. It is believed that silicon nanoparticle floating gate memory devices outperform conventional floating gate memory devices with faster read and write times, higher reliability, and lower power dissipation. The memory operation of nanoparticle field effect transistors depends on charge storage, similar to conventional non-volatile memory devices. In a nanoparticle non-volatile memory device, however, charge is not stored on a continuous floating gate polysilicon layer as in the conventional technology, but instead on a layer of discrete, preferably crystalline silicon nanoparticles which may alternatively be referred to as nanocrystals or quantum dots.

20 In these nanoparticle floating gate memory devices, the nanoparticles that act as charge storage elements are located within the gate oxide of a MOSFET. Injecting charge into the nanoparticles by tunneling from the channel alters the threshold voltage of the transistor. A normal write/read/erase cycle includes information being written by injecting charge from the channel into the nanoparticles, reading by measuring the subthreshold current-voltage characteristics, and erasing by removing charge from the particles to the channel. A single electron stored on each nanoparticle in an array with a nanoparticle density of $3\text{-}10 \times 10^{11}/\text{cm}^2$ results in a threshold voltage shift of 0.3-0.5 volts that is easily detected at room temperature. Generally speaking, as compared to conventional stacked-gate non-volatile memory devices, nanoparticle charge-storage offers several potential advantages, such as: (1) simple, low cost device fabrication since a dual-polysilicon process is not required; (2) superior retention characteristics resulting from Coulomb blockade and quantum confinement effects, enabling the

1 use of thinner tunnel oxides and lower operating voltages; (3) improved anti-punchthrough
performance due to the absence of drain-to-floating gate coupling thereby reducing drain induced
punchthrough, allowing higher drain voltages during readout, shorter channel lengths and
consequently a smaller cell area; and (4) excellent immunity to stress induced leakage current
5 (SILC) and defects, due to the distributed nature of the charge storage in the nanocrystal layer.
Even if a significant fraction of the individual nanocrystals that form the floating gate, are shorted
to the channel/substrate, the non-volatile memory device remains functional because the non-
shorted nanocrystals continue to store sufficient charge. The switching speed of devices made
of nanocrystal ensembles, however, is potentially limited by a distribution in charge transit times,
10 charging voltages, and threshold shifts resulting from various shortcomings of the nanoparticle
layer, such as the nanoparticle size and size distribution, nanoparticle density, layer planarity and
uniformity, and nanoparticle-to-nanoparticle interaction, i.e., lateral conduction.

Thus, there is a demonstrated need in the art for a layer of nanoparticles of uniform size
distribution and density. Similarly, there is a demonstrated need for fabricating silicon or silicon-
15 compatible nanocrystals with controlled size distributions and oxide thicknesses that can be
deposited on a substrate in a uniform and co-planar manner. It is also desirable to fabricate the
layer of nanocrystals using a process sequence that is simple, reliable, low cost, easily controlled,
repeatable, and free of contamination. Previous attempts at producing a layer of nanocrystals
suitable for use in a field-effect transistor or other non-volatile memory devices, include the
20 shortcomings of uncontrolled particle sizes, non-uniformity of particle deposition, high
contamination levels, low density of the particle material, non-uniform density of the particles
within the nanoparticle layer, and unpredictable planarity of the nanoparticle layer. Such
irregular and unpredictable nanocrystal layers result in poor-performing or non-functional
devices.

25 In conclusion, in order to produce non-volatile memory devices with faster read and write
times, higher reliability and lower power dissipation, it is desirable to produce nanocrystal
floating-gate non-volatile memory devices using a simple, low cost fabrication process which
provides a layer of nanocrystals which forms a monolayer of nanocrystals of uniform density and
particle size.

30 SUMMARY OF THE INVENTION

To address these and other needs and in view of its purposes, the present invention
provides a process for forming a stratum of semiconductor or metal particles having sizes in the
nanometer range and suitable for application as the floating gate in a non-volatile memory device.
35 The stratum is composed of particles having a tightly controlled range of particle sizes. The

1 process includes decomposing a source of semiconductor or metal material to form an aerosol
of nanoparticles, then sintering or heating the nanoparticles of the aerosol to convert the particles
to crystalline material. In an exemplary embodiment, the process may include quenching the
nanoparticle aerosol to minimize uncontrolled coagulation and to further control particle size. In
5 an exemplary embodiment, the majority of nanoparticles are single crystalline material. The
densified nanoparticles are compacted and include a density which approaches the bulk density
of the material of which they are formed. The densified nanoparticles may optionally be
classified by size, and particles outside the range of desired sizes are removed from the aerosol
stream.

10 The particles are preferably coated with a substantially continuous insulator coating to
produce particles having crystalline cores and a substantially continuous insulating shell. The
particles are then deposited onto a substrate surface using thermophoretic or other means. The
deposited, insulator-coated particles form a stratum on the substrate surface, and in one
embodiment, may be utilized as a floating gate in a non-volatile memory device. The particles
15 of the stratum are electrically isolated from one another.

BRIEF DESCRIPTION OF THE DRAWING

The invention is best understood from the following detailed description when read in
conjunction with the accompanying drawing. It is emphasized that, according to common
20 practice, the various features of the drawing are not to scale. On the contrary, the dimensions of
the various features and the relative dimensions and locations of the features are arbitrarily
expanded or reduced for clarity. Like numerals denote like features throughout the specification
and drawing. Included in the drawing are the following figures.

Figure 1 is a flow chart of an exemplary process sequence of the present invention;

25 Figure 2 is a schematic of an exemplary processing system of the present invention;

Figure 3 is a cross-sectional view of an exemplary pyrolysis furnace of the present
invention;

Figure 4 is a cross-sectional view of an exemplary radial differential mobility analyzer
used to classify nanoparticles in the present invention;

30 Figure 5 is a cross-sectional view of an exemplary thermophoretic deposition system of
the present invention;

Figure 6 is a cross-sectional view of an exemplary semiconductor nanoparticle of the
present invention;

35 Figure 7 is a perspective view showing a stratum of semiconductor nanoparticles formed
on a surface according to the present invention;

1 Figure 8 is a cross-sectional view of a stratum of semiconductor nanoparticles formed according to the present invention;

 Figure 9 is a cross-sectional view showing a stratum of semiconductor nanoparticles of the present invention interposed between exemplary oxide layers;

5 Figure 10 is a cross-sectional view showing the gate structure of an exemplary non-volatile floating gate field effect transistor according to the present invention;

 Figure 11 is a cross-sectional view of an exemplary non-volatile floating gate field effect transistor formed according to the present invention;

10 Figure 12 is a graph showing job sub-threshold characteristics of an exemplary MOSFET formed to include a floating gate formed of the exemplary silicon nanocrystals of the present invention;

 Figure 13 is a graph showing output characteristics of an exemplary MOSFET formed to include a floating gate formed of the exemplary silicon nanocrystals of the present invention;

15 Figure 14 is a graph showing programming transients of an exemplary MOSFET formed to include a floating gate formed of the exemplary silicon nanocrystals of the present invention;

 Figure 15 is a graph showing erase transients of an exemplary MOSFET formed to include a floating gate formed of the exemplary silicon nanocrystals of the present invention;

20 Figure 16 is a graph showing endurance characteristics of an exemplary MOSFET formed to include a floating gate formed of the exemplary silicon nanocrystals of the present invention; and

 Figure 17 is a graph showing retention and disturb characteristics of an exemplary MOSFET formed to include a floating gate formed of the exemplary silicon nanocrystals of the present invention.

25 DETAILED DESCRIPTION OF THE INVENTION

 The present invention provides an aerosol process to form semiconductor nanocrystals entrained in a gas, and to deposit them on a substrate. The process sequence includes pyrolyzing or otherwise decomposing a semiconductor material or precursor to form semiconductor nanoparticles and controlling processing conditions to prevent uncontrolled agglomeration of the nanoparticles. The nanoparticles formed as an aerosol, may preferably be sintered to convert the particles to dense crystalline material, again using processing conditions chosen to allow for a controlled rate of agglomeration and so as to preclude the formation of undesirable agglomerates of large particles. The sintering process densifies the particles such that the cores are characterized by a density which approaches the bulk density of the material of which they are formed. An aspect of the present invention is the controlled size distribution of the produced

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1 crystalline nanoparticles, the densified nature of the nanoparticles, and that the majority of
nanoparticles include a single-crystalline structure. The nanoparticles within the aerosol may
advantageously be classified according to size, such that the distribution of particle sizes is
tightened further. Nanoparticles which include sizes outside of a desired range of particle sizes
5 are removed from the aerosol prior to further processing. After classification, a dielectric shell
is formed on the nanoparticles and preferably encapsulates the cores. Thermal oxidation or other
methods may be used. The nanoparticles are then deposited on a substrate surface, such as over
the tunnel oxide of a non-volatile memory field effect transistor. The deposited, dielectric-coated
individual particles are electrically isolated from one another.

10 The particles may be deposited as a monolayer and they may be deposited to include a
particle density ranging from 10^{12} to 10^{13} particles/centimeter. They may be deposited such that
a significant portion of adjacent particles contact each other. The dielectric shells prevent lateral
shorting between such contacting particles. The deposition process may involve the formation
of a colloidal suspension of the particles, or thermophoretically or electrophoretically depositing
15 the particles directly onto a substrate. According to an exemplary embodiment, after the particles
are deposited on the substrate, they may be manipulated using force manipulation techniques in
an atomic force microscope or other equipment. In other exemplary embodiments, colloidal
forces and/or self-assembly techniques may be used to manipulate the deposited particles. The
manipulated particles may be arranged to form an ordered structure such as a wire.

20 Another aspect of this invention is a process to produce a stratum of metallic
nanoparticles consisting of metallic cores and dielectric coatings. The metallic nanoparticles are
substantially similar to the semiconductor nanoparticles described above, except that the core
materials are metal. The process for forming the metal nanoparticles and depositing the metal
nanoparticles on a substrate to form a stratum involves decomposing a metallic material or
25 precursor to form metallic nanoparticles entrained in a gas as an aerosol, then treating and
depositing the particles of the aerosol as described above in conjunction with semiconductor
nanoparticles.

The stratum of semiconductor nanocrystals or metal nanoparticles produced by the
present invention, is suitable for use as the floating gate of a floating gate transistor as well as for
30 other applications in various semiconductor and microelectronic devices. The stratum may be
characterized as a discontinuous floating gate when used as the floating gate of a transistor, and
finds particular application in non-volatile memory devices.

Now turning to the figures, Figure 1 shows an exemplary flow chart of the process of the
present invention. At step 400, an aerosol of semiconductor or metal nanoparticles is formed by
35 pyrolysis or other decomposition methods. At step 402, the nanoparticles contained within the

1 aerosol are sintered to form crystalline material. At optional step 404, the crystalized
nanoparticles are classified by size. Nanoparticles which fall outside of a pre-selected range of
particle sizes, are removed at 405B. The in-range nanoparticles are next delivered for dielectric
coating at 405A. At step 406, the nanoparticles are oxidized to form an oxide shell over the
5 nanoparticles, and at step 408 the nanoparticles of the aerosol are deposited on the substrate.

For brevity, the following detailed description will refer to the nanoparticles as
semiconductor nanoparticles, but it should be understood that the following description applies
to metal nanoparticles as well. With respect to embodiments specifically applicable to metal
nanoparticle formation and constitution, such will be pointed out.

10 Figure 2 shows a schematic of an exemplary arrangement of processing equipment used
to carry out the generalized process flow shown in Figure 1. The arrangement shown in Figure
2 is exemplary only as other and additional equipment may be used to carry out the process
according to the present invention. In the exemplary embodiment shown in Figure 2, pyrolysis
furnace 14, differential mobility analyzer 22 and oxidation furnace 32 are shown to be positioned
15 outside of clean room area 44 while deposition chamber 36 is shown to be positioned within
clean room area 44. Such arrangement is exemplary only and in alternative embodiments all of
the equipment may be included within a clean room environment. In the first step of the
exemplary processing operation, a semiconductor material or precursor is decomposed or broken
down to form smaller units of semiconductor particles. Various methods for decomposition of
20 the semiconductor material may be used, including gas evaporation, laser ablation, spark ablation,
pyrolysis and various other chemical reactions. According to the alternative embodiment in
which a metallic material or precursor is used to form metallic nanoparticles, gas evaporation,
laser ablation and spark ablation are advantageously utilized. Returning to the exemplary
semiconductor embodiment, the decomposition of the semiconductor material produces a
25 plurality of discrete semiconductor nanoparticles, so named because they typically include
particle sizes in the nanometer range. The semiconductor material from which the nanoparticles
are made by decomposition, may preferably be silicon but other semiconductor materials and
precursors and also other metallic materials and precursors may be used according to alternative
embodiments. Materials other than silicon are preferably selected for compatibility with silicon
30 processing. In an exemplary embodiment, a pyrolysis furnace is used to form the plurality of
discrete nanoparticles.

Referring to Figure 2, pyrolysis furnace 14 is fed by particle source gas 2 and diluent gas
4. In an exemplary embodiment, diluent gas source 12 may be nitrogen but other inert species
such as helium may be used according to alternative embodiments. In the exemplary
35 embodiment shown, diluent gas 4 is filtered by filter 8 and the diluent gas flow rate is controlled

1 by MFC (mass flow controller) 18. Particle source gas 2 includes the source of semiconductor
particles, preferably silicon, and includes a flow rate controlled by valve 6. Particle source gas
2 originates from source 10 and will preferably be a mixture also including a carrier gas. The
arrangement shown in Figure 2 is exemplary only and it should be understood that other gas flow
5 control means may be used. For example, the flow rate of particle source gas 2 may preferably
be controlled by an MFC (not shown). In an exemplary embodiment, each of diluent gas 4 and
the carrier gas may be nitrogen provided by a single source. The pyrolysis furnace 14 is shown
in greater detail in Figure 3.

Now turning to Figure 3, particle source gas 2 and diluent gas 4 are each delivered to
10 pyrolysis furnace 14. Particle source gas 2 includes a source from which the semiconductor
nanoparticles will be formed. In an exemplary embodiment, particle source gas 2 may include
silicon. In an exemplary embodiment, the silicon may be delivered as silane in particle source
gas 2. Gaseous silane may be considered a silicon precursor. According to other exemplary
embodiments, disilane or other silicon sources may be used alternatively. In an exemplary
15 embodiment, the carrier gas included within particle source gas 2 may be nitrogen, but other inert
carrier species may also be used. Diluent gas 4 will be nitrogen in the preferred embodiment, but
other inert gases may be used alternatively as the diluent gas. According to one exemplary
embodiment, the carrier gas and diluent gas may emanate from the same source. In a preferred
embodiment, each of the diluent gas and carrier species may be nitrogen and may be ultrahigh
20 purity (UHP) nitrogen which flows through an oxygen getter, then splits into two flows. One of
the flows becomes diluent gas 4 and the other flow serves as the carrier gas and flows along with
the semiconductor material in particle source gas 2. In an exemplary embodiment, each of
diluent gas 4 and particle source gas 2 may include a flow rate of 750 sccm. According to other
exemplary embodiments, the flow rates for each of diluent gas 4 and particle source gas 2 may
25 range from 650-850 sccm, but other flow rates may be used alternatively. According to a
preferred embodiment, particle source gas 2 includes 750 sccm of purified nitrogen as a carrier
gas in combination with less than 1 sccm of 5000 ppm silane in nitrogen. According to other
exemplary embodiments, other dilute mixtures of silane or other dilute mixtures of various other
semiconductor source gasses, may be used as particle source gas 2. Pyrolysis furnace 14 includes
30 maximum temperature zone 58 and pyrolysis zone 56. Pyrolysis furnace 14 is heated using
conventional heating means 52. The gas flows enter pyrolysis furnace 14 in the entry or pyrolysis
region 56 and flow downstream into the maximum temperature zone 58. The flows of each of
particle source gas 2 and diluent gas 4 may be delivered to pyrolysis furnace 14 through 1/8"
stainless steel tubing, but other tubing may be used according to other exemplary embodiments.
35 Within pyrolysis furnace 14, stainless steel tubing may be used or quartz tubing may be used.

1 In a preferred embodiment, particle source gas 2 is directed to pyrolysis furnace 14 through inner
tube 54 which is axially centered within outer tube 50 through which diluent gas 4 enters
pyrolysis furnace 14. In a preferred embodiment, the maximum temperature zone of pyrolysis
furnace 14 may be maintained at a temperature within the range of 950°C to 1150°C, and at
5 1050°C in the preferred embodiment. Other maximum temperatures may be used alternatively.

In the exemplary embodiment discussed herein, silane gas is the particle source and
silicon nanoparticles will be formed. It should be understood, however, that such is exemplary
and that other source gases, including other semiconductor or metal materials or precursors, may
be used to form other semiconductor or metal nanoparticles according to other exemplary
10 embodiments. Other exemplary source gasses may include GaAs, GaN or p-doped
semiconductor precursors.

Silane flow is introduced to pyrolysis furnace 14 as part of particle source gas 2 and flows
through pyrolysis zone 56 towards maximum temperature zone 58. The gas is heated in pyrolysis
zone 56 during a ramp-up period during which it is heated to the maximum temperature achieved
15 in maximum temperature zone 58. The silane pyrolyzes in the pyrolysis zone and breaks up into
a plurality of discrete silicon nanoparticles which form an aerosol. Stated alternatively, the
plurality of discrete semiconductor nanoparticles are entrained in a gas. The nanoparticles
initially form by homogeneous nucleation and grow by coagulation and vapor deposition. In an
exemplary embodiment, particle growth occurs during the ramp-up period during which the gas
20 is heated to the maximum temperature it achieves in the maximum temperature zone. In an
exemplary embodiment, particle growth occurs during a ramp-up period ranging from 10-50
milliseconds, preferably 30 milliseconds. Gas flow rates are chosen in conjunction with tubing
size and length of the pyrolysis zone to achieve a residence time of chosen duration in the
pyrolysis zone. During the ramp-up time within pyrolysis zone 56 of pyrolysis furnace 14, the
25 silane pyrolyzes to form an aerosol of silicon nanoparticles. Also during the ramp-up time within
pyrolysis zone 56 and before particle source gas 2 reaches maximum temperature zone 58, a
diluent stream preferably of UHP nitrogen combines in an annular flow around the aerosol
particle flow, upstream from the maximum temperature zone, to reduce particle concentration
and suppress particle coagulation. An exemplary arrangement shown in Figure 3 includes diluent
30 gas 4 entering through outer tube 50 to quench particle source gas 2 which enters through inner
tube 54, but other arrangements for mixing the respective gasses may be used alternatively.
Silicon aerosol particles with diameters ranging from 3-50 nanometers are produced by
controlling the flow rate of the dilute silane and the flow rates of the quenching ultrahigh purity
nitrogen or other gases. In a preferred embodiment, the diameters of each of the particles may
35 be less than 20 nanometers. The annular quenching flow also suppresses particle deposition onto

1 the tube walls and therefore reduces contamination. The flow of the gas mixture of the diluent gas and particle source gas 2 continues in the maximum temperature zone 58.

5 Within maximum temperature zone 58, the silicon nanoparticles are sintered so that they preferably become dense, spherical, single crystal nanoparticles. According to another exemplary embodiment, the densified nanoparticles may become polycrystalline particles. Flow conditions are chosen such that the sintering time may range from 200-600 milliseconds, preferably 400 milliseconds. During this densification/sintering process, it is essential that the reactor environment be oxygen-free since oxygen will cause the formation of silicon oxides rather than crystalline silicon. Additionally, oxygen prevents the desirable sintering of silicon nanoparticles.

10 The sintering is carried out in a controlled fashion to suppress uncontrolled coagulation of the particles and therefore to maintain the size distribution of the particles within a tight range. During this sintering process, the particles are heated to a sufficiently high temperature to density the particles to form highly compacted particles, and to crystallize the particles. The densified, discrete particles are formed to have a density which is substantially as great as the bulk density

15 of the pure semiconductor material of which they are formed. The bulk density of a material is the maximum density of the material at standard temperature and pressure (STP) conditions. Moreover, a majority of the densified particles will be single crystalline material. In a preferred embodiment, all of the densified particles will be single crystalline material. Also in the preferred embodiment, the densified particles will be generally spherical in shape. Aerosol stream 16, which includes the silicon nanocrystals, exits pyrolysis furnace 14. According to another exemplary embodiment in which single crystalline particles are not needed, the sintering process may be bypassed. After the sintering process, particle diameters may range from 3-50 nanometers, preferably less than 20 nanometers.

25 Once formed and sintered, the densified silicon nanoparticles or nanocrystals of the aerosol may advantageously be charged and classified by a size. The classification may be accomplished by time-of-flight separations of a focused particle beam. Figure 2 shows aerosol stream 16 being delivered to an exemplary differential mobility analyzer (DMA) 22 used to classify the nanoparticles. Aerosol stream 16 may optionally be cooled prior to classification, using conventional means. Within DMA 22, the nanoparticles within the aerosol are separated

30 and out-of-range nanoparticles are removed from the DMA 22 in out-of-range nanoparticle stream 24, while classified particles within a pre-selected range of sizes continue to flow in stream 26 for additional processing. DMA 22 is shown in greater detail in Figure 4.

To positively charge the nanoparticles for classification, they may be passed through a so-called aerosol neutralizer prior to delivery to DMA 22. In the aerosol neutralizer, the particles

35 are exposed to an ambipolar cloud of gas ions produced by a Kr source, in an exemplary

1 embodiment. During this process, a small fraction of the nanoparticles become charged with most carrying a single charge. Other devices for charging the nanoparticles may be used for classification, particularly ones that change a larger fraction of the particles.

Now turning to Figure 4, radial DMA 22 is a parallel-plate capacitor with radial symmetry
5 in an exemplary embodiment. According to other exemplary embodiments, DMA 22 may take on other configurations. Generally speaking, an electric field is applied to the plates of the differential mobility analyzer 22 to separate the charged nanoparticles and to allow for particles having diameters within a pre-selected range of particle sizes, to exit DMA 22 and continue processing. In the exemplary embodiment shown, an electric field is applied across electrodes
10 62 and 64. Particle separation occurs due to electromigration of particles within DMA 22. The desired, pre-selected particle range may vary according to various exemplary embodiments. Positively charged nanoparticles within aerosol stream 16 enter DMA 22 tangentially, through aerosol inlet port 25 and migrate radially inward along a particle-free laminar sheath flow 66 in the presence of an applied negative electric field. Ideally, the nanoparticles carry only one
15 elementary charge, and since these entering particles are generally spherical, their mobility is related to their diameter. Nanoparticles with different sizes follow different trajectories 68 within DMA 22. At the center of DMA 22 is sampling port 27 through which the classified nanoparticles within the pre-selected size range, are removed. Uncharged nanoparticles and nanoparticles with sizes larger than the classified size exit DMA 22 with an excess flow as part
20 of exhaust flow 24. Particles which are smaller than the classified particles in the pre-selected range deposit on the bottom electrode of DMA 22. The diameter of the nanoparticles which are transmitted in classified sample flow 26 is controlled and determined by flow rates and the applied voltage.

The particle concentration within the aerosol stream can be monitored throughout the
25 synthesis process by flowing a portion of the classified aerosol flow into an electrometer with femtoampere sensitivity. By varying the voltage applied to DMA 22 and detecting the particle concentration from the electrometer read downstream from DMA 22, for example, the particle size of the silicon nanoparticles exiting the furnace can be measured.

In an exemplary embodiment, particle diameters may be chosen to lie within the range
30 of 2-10 nanometers, but other ranges such as 2-6 nanometers, 3-7 nanometers, 5-10 nanometers, or less than 15 nanometers, may be chosen alternatively. In another exemplary embodiment, nanoparticles within the 1 to 10 nanometer diameter size range may be classified within about 6% on diameter. According to another exemplary embodiment, the nanoparticles may be classified such that 90% of the particles are within the desired range.

1 In cases where a thermal oxide passivating layer is desired, classified particle flow 26 is
next delivered to oxidation furnace 32 along with oxygen stream 29 as shown in Figure 2.
Oxygen source 28 and therefore oxygen flow 29 may be controlled by MFC 30 and include an
oxygen concentration of 20% oxygen in nitrogen in an exemplary embodiment. Oxidation may
5 occur as the silicon nanoparticle aerosol is combined with a controlled flow of oxygen or the
silicon nanoparticle aerosol may be flowed through a water evaporator. According to yet another
exemplary embodiment, oxidation may take place using TEOS (tetraethyl orthosilicate).
According to still other exemplary embodiments, dielectric or insulating layers other than an
oxide may be formed to coat the individual nanoparticles to insure that the individual
10 nanoparticles are electrically isolated from one another. The insulating-layer coated particles are
preferably encapsulated by the insulating-layer coating.

In the oxidation furnace/oxygen flow embodiment shown in Figure 2, since the silicon
nanoparticles are produced in ultra high purity nitrogen, the oxygen flow rate can be changed to
alter the concentration of oxygen in the final oxygen/nitrogen mixture. Various oxygen flow
15 rates may be used. The oxidation temperature within oxidation furnace 32 can also be varied.
Typical oxidation furnace temperatures lie in the range of 700-1100°C with residence times of
200-800 milliseconds. Oxidation temperatures within oxidation furnace 32 are chosen in this
range because lower temperatures produce poorer quality oxides, whereas higher temperatures
have the tendency to evaporate silicon dioxide that is formed on the surface of the silicon
20 nanoparticles. During the oxidation process which may occur at 900°C in an exemplary
embodiment, a thermal oxide shell forms on the exposed silicon surface of the silicon
nanoparticles, partially consuming the outer silicon material during the reaction. The thickness
of the oxide shell is controlled by controlling the residence time of the aerosol within oxidation
furnace 32. In general, a longer residence time increases oxide shell thickness. Oxide shell
25 thicknesses typically range from 1-10 nanometers, and in a preferred embodiment may be
controlled within the range of 1.5-2.0 nanometers. The thermal oxidation process is a uniform
process which consumes the silicon surface of the preferably crystallized silicon nanoparticles
thereby reducing the "core" size of the silicon nanoparticle. After oxidation, the silicon
nanoparticles preferably include a crystalline silicon core having a diameter uniformly reduced
30 with respect to the diameter of the silicon particle prior to oxidation. The silicon nanoparticle
also includes an oxide shell surrounding the silicon core. This will be shown in Figure 6.

According to another exemplary embodiment, other materials such as water can be used
to oxidize the silicon nanoparticles in a hot tube furnace, a process known as steam oxidation.
According to this embodiment, the aerosol of silicon nanoparticles flows through a water
35 evaporator (not shown) maintained at a controlled but variable temperature to control the amount

1 of water allowed into the oxidation furnace. The water concentration can be controlled by varying the aerosol flow rate through the water evaporator. After the water evaporator, the aerosol and water are flowed through a high temperature oxidation furnace where the particles become oxide passivated at temperatures of 700°C-1000°C.

5 According to yet another exemplary embodiment, the silicon nanoparticles may be coated with silica by chemical vapor deposition using TEOS (tetraethyl orthosilicate) or other SiO₂ precursors such as TMOS (tetramethyl orthosilicate). Using the TEOS oxidation process, the particle core size is not reduced as silicon material is not consumed during the deposition of a silicon dioxide film onto the classified silicon nanoparticles using TEOS as the precursor. The
10 deposition process allows the possibility of producing oxide-passivated silicon nanoparticles while retaining the silicon core diameter such that it will not differ significantly from the original classified core diameter. To produce silicon nanoparticles which are uniformly coated with a silicon dioxide film, temperatures below about 750°C are used. In an exemplary embodiment, using oxidation temperatures ranging from 500°C to 700°C, an oxide thickness of about 0.6nm
15 is uniformly deposited on the particles. Under certain circumstances, the TEOS does not form a uniform layer around the particle, rather, the TEOS does not wet the silicon surface and, thus, balls up on the particle surface. When introduced into the oxidation furnace, the TEOS ball then reacts to produce silicon dioxide and the final particle morphology is the originally classified silicon nanoparticle with a silicon dioxide particle attached to its surface. To prevent this
20 undesirable particle morphology, it is necessary to pre-treat the silicon nanoparticle surface. One pre-treatment method is to expose the nanoparticle aerosol to ethanol vapor but other materials such as methanol or isopropanol may be used in other exemplary embodiments. This involves flowing the aerosol through an ethanol evaporator maintained at a constant temperature to control the amount of ethanol introduced into the aerosol flow. This pre-treatment technique has been
25 found to be particularly advantageous for TEOS oxide passivation performed at temperatures below about 500°C.

According to other exemplary embodiments, other chemical vapor deposition methods and other methods for causing the surface of the nanoparticles to react with a gas may be used. Various dielectric or insulating layers may be formed substantially continuously over the
30 nanoparticle surface, thereby forming a dielectric shell of sorts.

After the silicon nanocrystals have preferably been coated with a dielectric coating according to one of the exemplary methods, the particles are collected for subsequent use in device fabrication. According to one exemplary embodiment, the particles may be directly deposited onto a device substrate and, according to another exemplary embodiment, the particles
35 may be collected in liquid for subsequent colloidal processing. The former approach has the

1 advantage of minimizing potential contamination and ease of interfacing with the scanning probe
microscope and other dry manipulation techniques. The latter approach offers the potential to
use colloidal forces to assist in the assembly of the classified, passivated silicon nanoparticles
into the desired device structures. Several techniques for forming two-dimensional monolayer
5 arrays of silicon nanoparticles from stabilized colloids are available. In an exemplary
embodiment, electrophoretic or electrostatic deposition may be used. According to
electrophoretic deposition, charged particles are caused to migrate by application of an electric
field and to be deposited on a surface.

According to one exemplary embodiment, conventional electrophoretic deposition
10 techniques may be used to deposit the exemplary oxidized nanoparticles directly onto a substrate
surface. According to another exemplary embodiment, deposition may be accomplished by
inertial impaction. In yet another exemplary embodiment such as shown in Figure 2,
thermophoretic deposition techniques may be used to deposit the silicon nanoparticles from the
oxidized aerosol directly onto a substrate surface. Figure 2 shows exemplary oxidized particle
15 stream 34 being delivered to thermophoretic deposition chamber 36. Thermophoretic deposition
chamber 36 includes water inlet 38 and water outlet 40 to cool the substrate within the
thermophoretic deposition chamber. Thermophoretic deposition chamber 36 is shown in more
detail in Figure 5.

Now turning to Figure 5, thermophoretic deposition chamber 36 includes aerosol inlet
20 port 35 through which oxidized particle stream 34 enters thermophoretic deposition chamber 36.
In the exemplary deposition chamber shown in Figure 5, aerosol oxidized particle stream 34
enters the chamber centrally and moves radially outward through the chamber and exits as gas
outlet stream 84. Substrate 74 including substrate surface 76 rests on water-cooled disk 86.
Water-cooled disk 86 is cooled by cooling water which enters as inlet water 38 and exits as outlet
25 water 40 and is preferably maintained at a temperature of 23 °C, although other temperatures may
be used according to other exemplary embodiments. Moreover, various other suitable methods
may be used to cool the underside of substrate 74 and to maintain it at a significantly lower
temperature than other portions of the deposition chamber. The top of the deposition chamber
is heated to 200 °C using conventional means in an exemplary embodiment, although other
30 temperatures may be used according to other exemplary embodiments. This provides an effective
temperature difference of 177 °C. According to various other exemplary embodiments,
temperature differences in the deposition chamber may be about 150 °C, 175 °C, 200 °C, or
values therebetween. In a preferred embodiment, the temperature difference between portions
of the preferably metal deposition chamber and the water-cooled disk 86 may be at least 170 °C.
35 Since the nanoparticles within the aerosol move from high temperatures to cooler temperatures,

1 the particles deposit on surface 76 of substrate 74. To preclude any contact between the
deposition chamber and the substrate 74, substrate 74 may be supported by quartz pegs 82 in an
exemplary embodiment. According to other exemplary embodiments, quartz pegs 82 may not
be needed. In a preferred embodiment, substrate 74 may be a silicon wafer commonly used in
5 the semiconductor manufacturing industry and surface 76 may include the substructure of a
device onto which a monolayer of silicon nanocrystals is preferably deposited. According to
other exemplary embodiments, other substrates upon which semiconductor or microelectronic
devices will be formed, may be used. Thermophoretic deposition chamber 36 may be sized to
accommodate various sizes of substrates 74 such as a 6" silicon wafer, an 8" silicon wafer, and
10 other substrates of various sizes.

The thermophoretically deposited layer of silicon nanoparticles may be characterized as
a stratum composed of a monolayer of nanoparticles or simply as a discontinuous layer of silicon.
In an exemplary embodiment, particle densities may range from 10^{12} to 10^{13} particles per square
centimeter.

15 Figures 6-10 show various characteristics of the stratum of oxidized discrete silicon
nanoparticles. Figure 6 is a cross-sectional view showing a single nanoparticle 100.
Nanoparticle 100 includes core 102 and oxide shell 106. Each of core 102 and nanoparticle 100
are preferably spherical in shape. In an exemplary embodiment, diameter 104 of core 102 may
be less than 15 nanometers and may range from 2-10 nanometers, most preferably 3-7
20 nanometers, according to various exemplary embodiments. In an exemplary embodiment, at least
90% of the cores will include a diameter between 2 and 10 nanometers. Dielectric shell 106 may
include a thickness ranging from 1-10 nanometers and will include a uniform thickness of 1.5
to 2.0 nanometers in an exemplary embodiment. In a preferred embodiment, dielectric shell 106
will be an oxide shell. Dielectric shell 106 is a continuous dielectric coating which envelopes
25 core 102. In an exemplary embodiment, silicon core 102 may represent 30-75% of the volume
of silicon nanoparticle 100, including oxide shell 106. Core 102 is formed of a semiconductor
material compatible with silicon processing. In the preferred embodiment, core 102 is formed
of silicon, and will preferably be a crystalline silicon material. In a preferred embodiment, core
102 will be a single crystalline material. Core 102 includes a density at or near the bulk density
30 of the pure semiconductor material of which it is formed. The bulk density of a material is the
maximum density of the material at standard temperature and pressure (STP) conditions.

Now turning to Figure 7, a perspective view of stratum 101 of a plurality of
semiconductor nanoparticles 100 is shown as being formed on substrate surface 76. The
nanoparticles which make up stratum 101 are as described in Figure 6. An aspect of the present
35 invention is the uniformity of density of the semiconductor nanoparticles within stratum 101.

1 Density may range from 10^{12} to 10^{13} particles/cm² but other densities may be used according to
other exemplary embodiments. The stratum 101 is essentially a monolayer of discrete
nanoparticles. A plurality of the discrete nanoparticles, such as exemplary nanoparticles 111 and
113, contact each other. In the preferred embodiment, the majority of adjacent nanoparticles may
5 contact each other. It is an advantage of the present invention that the individual nanoparticles
that are each capable of storing an electrical charge, are electrically isolated from one another,
even if in contact. This is attributable to the presence of the dielectric coating formed on the
particles prior to deposition on the substrate. Because of the ultra high purity nitrogen used and
the cleaning techniques used to maintain the processing equipment in an ultra clean state, the
10 density of foreign particle contamination on surface 76 and therefore in stratum 101, due to the
deposition of stratum 101, may be less than 10^{11} atoms per square centimeter. The discrete
nanoparticles of stratum 101 are characterized by a tightly controlled range of particle sizes.
According to one exemplary embodiment, the nanoparticle cores may be less than 15 nanometers.
According to an exemplary embodiment, the nanoparticles may be essentially the same size.
15 According to an exemplary embodiment, particle sizes of the nanoparticles of stratum 101
include a particle size distribution that is approximately log-normal with respect to diameter, with
a geometric standard deviation less than 1.5. The log-normal distribution is well-known in the
art and is used to describe a population of samples that is normally distributed with respect to the
logarithm of the distribution parameter (e.g., diameter). In an exemplary embodiment, the
20 nanoparticles may have an average core diameter within the range of 2-10 nanometers or 3-7
nanometers and, also in an exemplary embodiment, at least 90% of the cores will include a
diameter within the range of 3-7 nanometers. As noted above, cores 102, such as shown in
Figure 6, are preferably formed of single crystal material such that the semiconductor
nanoparticle may be referred to as a nanocrystal. According to yet another exemplary
25 embodiment, at least 90% of the cores of the discrete semiconductor nanoparticles may lie within
a range of 2-6 nanometers, or 90% of the cores may be less than 10 nanometers.

Figure 8 shows a cross-sectional view of a preferred embodiment of stratum 101. As
shown in Figure 8, the plurality of adjacent nanoparticles 100 contact each other laterally.
Because of oxide shells 106 formed on each nanoparticle 100, adjacent semiconductor cores 102
30 are electrically insulated from one another and lateral shorting is precluded.

In the subsequent description, semiconductor nanoparticles 100 will be referred to as
silicon nanoparticles, but the reader is reminded that such is exemplary only. Semiconductor
nanoparticles 100 may be formed of other semiconductor or metal materials, alternatively. Figure
9 is a cross-sectional view showing stratum 101 of silicon nanoparticles formed between
35 subjacent oxide layer 153 and superjacent oxide layer 151. Stratum 101 is as shown and

1 described in conjunction with Figures 7 and 8 and includes silicon nanoparticles as shown and
described in Figure 6. According to this exemplary embodiment, cores 102 essentially function
as a discontinuous layer of silicon nanoparticles, each surrounded by an oxide including the oxide
shells (present, but not distinguishable in Figure 9) and the subjacent and superjacent oxide
5 layers. The oxide shell serves to electrically insulate silicon cores 102 from one another in a
monolayer formed within an oxide film formed over surface 155.

According to another exemplary embodiment, force manipulation of the deposited silicon
nanoparticles may be carried out. In an exemplary embodiment, contact mode atomic force
microscopy may be used to move nanocrystals that were initially in spatially random positions
10 such as deposited and as shown in Figure 7. An ordered structure of nanocrystal "wires" and
other ordered arrays may be produced using this technique. Colloidal forces and self-assembly
may alternatively be used to produce ordered deposits.

According to a preferred embodiment, the stratum of silicon nanoparticles including
highly controlled particle sizes, densities and of superior uniformity may be utilized as the
15 floating gate of a non-volatile memory, floating gate transistor. According to this embodiment,
the stratum of silicon nanoparticles is formed over an oxide, referred to as a tunnel oxide, formed
over gate regions of transistors. Figure 10 shows such an exemplary structure after the various
layers have been formed and the layers patterned to form a gate structure. In Figure 10, tunnel
oxide film 124 is formed over surface 76 of substrate 74 including over gate area 120. Stratum
20 101 of silicon nanoparticles, including cores 102, is formed over tunnel oxide 124. Upper gate
oxide film 128 and gate electrode film 132 are next sequentially formed. After the sequence of
films are formed over one another, including over gate area 120, situated between source/drain
regions 122, conventional patterning and etching means are used to define the gate region and
to form gate electrode structure 140. A plurality of such structures are preferably formed
25 simultaneously according to the above process.

Gate structure 140 includes gate width 136, which may be less than 0.2 microns.
According to one exemplary embodiment, gate width 136 may range from 0.18 microns to 1.2
microns, but other gate widths may be used according to other exemplary embodiments.
Thickness 126 of tunnel oxide film 124 and thickness 130 of upper gate oxide film 128 are
30 chosen in conjunction with the oxide shell thickness formed around each of the silicon
nanoparticles in stratum 101. The thicknesses are chosen such that the total, or effective tunnel
oxide thickness 127, lies within the range of 3-12 nanometers and in a preferred embodiment may
lie within the range of 4-8 nanometers. According to one exemplary embodiment, thickness 126
may be 3-12 nanometers, or preferably 3-6 nanometers. Similarly, thickness 130 of upper gate
35 oxide film 128 is chosen so that total, or effective thickness 129 of the upper gate oxide lies

1 within the range of 6-15 nanometers. In an exemplary embodiment, thickness 130 or effective
thickness 129 may lie within the range of 10-15 nanometers, but other thicknesses sufficient to
preclude electrons exchanging between cores 102 and gate electrode 132 may be used
alternatively. Various conventional films suitable for use as gate electrode 132 may be used and
5 may be formed to various suitable thicknesses 134. Transistor gate structure 140 is formed over
channel region 120 and between source/drain regions 122. According to other exemplary
embodiments, each of tunnel oxide film 124 and upper gate oxide 128 may be formed of other
dielectric materials. As discussed previously, the discrete silicon nanoparticles of stratum 101
10 may be of various dimensions and will preferably be crystallized silicon. Stratum 101 may
alternatively be described as a discontinuous floating gate of gate structure 140. Particle size may
be chosen in conjunction with gate width 136. In an exemplary embodiment, the total diameter
of a silicon nanoparticle 100, including oxide shell 106, will be chosen to be less than $0.1 \times$ gate
width 136. In this manner, at least ten silicon nanoparticles will be included within stratum 101
across gate width 136. Additionally, the non-volatile memory transistor formed to include gate
15 structure 140 will include a length (depth into and out of the plane of the drawing) ranging from
10-100 microns long according to an exemplary embodiment. Other transistor lengths may be
used alternatively.

Now turning to Figure 11, floating gate transistor 162 is shown and includes gate structure
140. Floating gate transistor 162 is formed to include stratum 101 of aerosol silicon
20 nanoparticles, and features program/erase characteristics comparable to conventional stacked gate
non-volatile memory devices, excellent endurance (greater than 10^5 program/erase cycles), and
long-term non-volatility, even when a thin bottom oxide 124 of less than 6 nanometers is used.
The reader is reminded that stratum 101 may be formed of nanoparticles formed of other
semiconductor or metal materials, in other exemplary embodiments. Floating gate transistor 162
25 includes source/drain contacts 154 formed through dielectric material 152, and may be
electrically coupled, biased and tested through power supplies 150, 156, 158 and 160. Power
supply 150 is used to bias gate electrode 132, power supplies 156 and 158 are connected to the
source/drain regions 122, and power supply 160 is coupled to substrate 74 and channel region
120. Other conventional arrangements may be used for biasing exemplary transistor 162 and
30 conventional means may be used for programming, erasing and testing transistor 162.

Typical subthreshold and output characteristics of exemplary aerosol-silicon nanocrystal
field effect transistors are shown in Figures 12 and 13, respectively. Figure 12 is a graph of the
drive current, I_d , versus gate voltage, V_{gate} , and Figure 13 is a graph of the drive current versus
drain voltage, V_{DRAIN} . The values of the subthreshold slope (200mv/dec), and the DIBL
35 (100mv/v) and the drive current (30 microamps/micron), are typical for thick gate dielectric, high

1 substrate doped non-volatile memory devices. The threshold voltage, V_t , has been defined as the
gate voltage corresponding to a drain-source current of $1 \mu\text{A}$ when a drain bias of 1 volt is
applied. Uniform Fowler-Nordheim tunneling has been used for both the program and the erase
operation, though programming using channel hot-electron injection is possible as well.
5 Programming at source and drain separately also allows multi-bit storage in one device.

Figure 14 is a graph of threshold voltage versus time and shows programming transients
for various gate voltages V_g , using a substrate bias of -5V. Figure 15 is a graph of threshold
voltage versus time and shows erase transients for various V_g 's, using a substrate bias of -8V.
As shown in Figures 14, 15, 16 and 17, the high areal nanocrystal-density obtained by the aerosol
10 fabrication process results in a large threshold voltage window of at least two volts. The device
programs to a high V_t of about +3.3 volts in $50 \mu\text{s}$ with gate and substrate bias of +8V and -5V,
respectively. The device erases to a low V_t of about +1V in 100ms with gate and substrate bias
of +8V and -8V, respectively. According to this exemplary embodiment, the threshold voltage
window is about 2.3 volts, but other threshold voltage windows may be produced according to
15 other exemplary embodiments.

Figure 16 is a graph indicative of endurance characteristics and showing the program and
erase V_t as a function of number of program/erase cycles. As shown in Figure 16, the aerosol
non-volatile memory devices feature excellent endurance behavior as demonstrated by the small
 V_t window closure observed after 5×10^5 program/erase cycles. It can be seen that less than a
20 15% closure of the program/erase V_t window is observable after 5×10^5 program/erase cycles.
The gradual shift of the V_t window to higher threshold voltages is indicative of charge being built
up in the gate oxide layer during cycling. Additionally, in spite of thin tunnel oxides used,
reasonable disturb times and long non-volatility is obtained indicative of intrinsic advantages of
nanocrystal charge storage. No stress induced leakage current has been observed. No drain
25 disturb was detected even using drain voltages as high as 4 volts, which is indicative of the
absence of lateral conduction between the nanocrystals in stratum 101.

Figure 17 is a graph showing retention and disturb characteristics (threshold voltage - V_t ,
versus time) of an exemplary MOSFET formed to include a floating gate formed of exemplary
silicon nanocrystals of the present invention.

30 The preceding merely illustrates the principles of the invention. It will thus be
appreciated that those skilled in the art will be able to devise various arrangements which,
although not explicitly described or shown herein, embody the principles of the invention and
are included within its spirit and scope. For example, the present invention can be used to
provide various and multiple strata of silicon and other semiconductor nanoparticles for various
35 applications in the semiconductor/microelectronics industry. According to various exemplary

1 embodiments, multiple strata of various nanoparticles may be formed directly on one another according to the process of the present invention.

5 All examples and conditional language recited herein are principally intended expressly to be only for pedagogical purposes and to aid the reader in understanding the principals of the invention and the concepts contributed by the inventors to furthering the art, and are to be construed as being without limitation to such specifically recited examples and conditions. Moreover, all statements herein reciting principles, aspects, and embodiments of the invention, as well as specific examples thereof, are intended to encompass both structural and functional equivalents thereof. Additionally, it is intended that such equivalents include both currently 10 known equivalents such as equivalents developed in the future, i.e., any elements developed that perform the same function, regardless of structure. The scope of the present invention, therefore, is not intended to be limited to the exemplary embodiments shown and described herein. Rather, the scope and spirit of the present invention is embodied by the appended claims.

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1 WHAT IS CLAIMED IS:

1. A method for forming a stratum consisting of semiconductor particles, comprising the steps of:

5 a) forming an original plurality of discrete semiconductor particles from one of a source of semiconductor material and a precursor for said semiconductor material, said original plurality of discrete semiconductor particles entrained in a gas and thereby forming an aerosol;

10 b) heating said aerosol to a sufficiently high temperature to densify said particles such that substantially all of said particles include a density substantially as great as the bulk density of said semiconductor material and thereby forming a corresponding plurality of densified discrete semiconductor particles entrained in a gas;

c) forming an electrically insulating cover on each of said particles, thereby forming a corresponding plurality of insulator-coated densified discrete semiconductor particles; and

15 d) depositing said plurality of insulator-coated densified discrete semiconductor particles on a substrate thereby forming a stratum of discrete, electrically isolated semiconductor particles on said substrate.

2. The method as in claim 1, in which step a) includes pyrolyzing a gas.

20 3. The method as in claim 2, in which step a) includes said pyrolyzing occurring during a ramp-up period ranging from 10-50 msec, during which said gas is heated to a maximum temperature.

25 4. The method as in claim 3, in which said maximum temperature lies within the range of 950°C to 1150°C.

5. The method as in claim 3, in which said gas flows through a pyrolysis furnace at a flow rate ranging from 650 to 850 sccm during said ramp-up period.

30 6. The method as in claim 3, in which step a) includes intermixing said gas with a diluent gas prior to said gas attaining said maximum temperature.

7. The method as in claim 3, further comprising maintaining said gas at said maximum temperature during said step of heating for a time ranging from 200 msec to 600 msec.

- 1 8. The method as in claim 1, in which said step b) includes said heating converting a majority of said original plurality of discrete semiconductor particles to single crystalline material, said heating occurring at a sintering temperature within the range of 950°C to 1150°C.
- 5 9. The method as in claim 8, in which step a) includes pyrolyzing a gas during a ramp-up period ranging from 10-50 msec, during which said gas is heated to said sintering temperature and intermixed with a diluent gas to form a gas mixture, and said step b) includes said gas mixture having a flow rate ranging from 1300 sccm to 1700 sccm.
- 10 10. The method as in claim 1, in which step c) comprises thermal oxidation and said cover comprises an oxide cover.
11. The method as in claim 1, in which step c) comprises chemical vapor deposition.
- 15 12. The method as in claim 1, in which step c) includes reacting surfaces of said particles with a gas.
13. The method as in claim 1, in which step c) comprises depositing silicon dioxide on said semiconductor particles using TEOS (tetraethyl orthosilicate).
- 20 14. The method as in claim 13, in which said depositing silicon dioxide using TEOS takes place at a temperature no greater than 750°C.
- 25 15. The method as in claim 1, in which said original plurality of discrete semiconductor particles comprise silicon particles and said insulator-coated densified discrete semiconductor particles each include a silicon core and a silicon dioxide shell.
- 30 16. The method as in claim 2, in which said step a) includes delivering said gas to a pyrolysis furnace in the form of a gas stream, said gas stream including a mixture of a carrier gas having a flow rate within the range of 650 sccm to 850 sccm, and silane gas and including about 5000 ppm of silane in nitrogen and having a flow rate less than 1 sccm.
- 35 17. The method as in claim 2, in which said gas includes silane and a carrier species, and said step a) includes delivering said gas and a diluent gas to a pyrolysis furnace.

- 1 18. The method as in claim 17, in which said diluent gas comprises nitrogen.
19. The method as in claim 17, in which said gas is delivered within a tube axially disposed within a further tube, said diluent gas is delivered within said further tube, and said gas and said
5 diluent gas are allowed to intermix within said pyrolysis furnace.
20. The method as in claim 1, further comprising the step of classifying particles of said plurality of densified discrete semiconductor particles after step b), and directing a classified plurality of densified discrete semiconductor particles within a pre-selected range of sizes for
10 further processing.
21. The method as in claim 20, in which said pre-selected range of sizes includes particles having average diameters within the range of 5-10 nm.
- 15 22. The method as in claim 20, in which said step of classifying includes applying an electric field to a differential mobility analyzer.
23. The method as in claim 20, in which said step of classifying includes time-of-flight separation of a focused particle beam.
20
24. The method as in claim 20, further comprising cooling said discrete semiconductor particles after said step of heating and prior to said step of classifying.
25. The method as in claim 1, in which step d) comprises delivering said plurality of
25 insulator-coated densified discrete semiconductor particles to a deposition chamber including said substrate therein, and thermophoretically depositing said plurality of insulator-coated densified discrete semiconductor particles on said substrate.
26. The method as in claim 25, in which step d) includes maintaining said substrate at a
30 temperature which is at least 175°C cooler than internal portions of said deposition chamber.
27. The method as in claim 1, in which step d) includes thermophoretically depositing said stratum to include a density of 10^{12} - 10^{13} particles/cm².
- 35

1 28. The method as in claim 1, in which step d) produces said stratum which is characterized by a foreign contamination level being less than 10^{11} atoms/cm².

5 29. The method as in claim 1, in which said substrate includes a dielectric layer formed thereon and said step d) comprises depositing said insulator-coated densified discrete semiconductor particles on said dielectric layer, thereby forming said stratum over said dielectric layer.

10 30. The method as in claim 29, in which said dielectric layer comprises a tunnel oxide and further comprising the steps of:

forming a gate dielectric film over said stratum;

forming a gate electrode over said gate dielectric film; and

defining a gate region and removing portions of said gate electrode, said gate dielectric film, said stratum, and said tunnel oxide from regions outside of said gate region.

15 31. The method as in claim 30, in which said tunnel oxide includes a thickness within the range of 3 to 12 nanometers.

20 32. The method as in claim 1, in which step d) includes said stratum being essentially a monolayer of said oxidized semiconductor particles.

33. The method as in claim 1, in which step d) includes:

introducing said plurality of insulator-coated densified discrete semiconductor particles into a liquid medium to form a colloid; and

25 electrophoretically depositing said plurality of insulator-coated densified discrete semiconductor particles onto a surface of said substrate.

34. The method as in claim 1, in which step d) includes:

30 delivering said plurality of insulator-coated densified discrete semiconductor particles to a deposition chamber which includes said substrate therein; and

forming an ordered structure of said plurality of insulator-coated densified discrete semiconductor particles on said substrate, using contact mode atomic force microscopy.

35 35. The method as in claim 34, in which said step d) comprises forming a wire of said insulator-coated densified discrete semiconductor particles.

1 36. A method for forming a stratum of a plurality of discrete nanoparticles, comprising the steps of:

a) decomposing a material to produce an original plurality of discrete metal nanoparticles entrained in a gas and thereby forming an aerosol;

5 b) classifying particles of said original plurality of discrete metal nanoparticles by size, and delivering a classified plurality of discrete metal nanoparticles within a pre-selected range of sizes for further processing;

c) forming an electrically insulating cover on each of said particles thereby forming a corresponding plurality of insulator-covered nanoparticles;

10 d) delivering said plurality of insulator-covered nanoparticles to a deposition chamber which includes a substrate therein; and

e) thermophoretically depositing said plurality of insulator-covered nanoparticles on said substrate thereby forming a stratum of discrete insulator-covered nanoparticles on said substrate.

15 37. The method as in claim 36, in which step a) comprises spark ablation.

38. The method as in claim 36, in which step a) comprises laser ablation.

20 39. The method as in claim 36, in which step a) comprises gas evaporation.

40. A method for forming a stratum consisting of semiconductor particles, comprising the steps of:

25 pyrolyzing a particle source gas to produce an original plurality of discrete semiconductor particles;

quenching said particle source gas with a diluent gas during said step of pyrolyzing;

classifying particles of said original plurality of discrete semiconductor nanoparticles by size and directing a classified plurality of said discrete semiconductor particles to a deposition chamber which includes a substrate therein; and

30 thermophoretically depositing said classified plurality of said discrete semiconductor particles on said substrate thereby forming a discontinuous layer of said discrete semiconductor particles on said substrate.

1 41. The method as in claim 40, further comprising the step of sintering said original plurality of discrete semiconductor particles to form a corresponding plurality of crystalline semiconductor particles.

5 42. The method as in claim 1, wherein said step c) comprises encapsulating said particles.

43. The method as in claim 1, in which step a) includes forming said original plurality of discrete semiconductor particles to have diameters less than 20 nanometers.

10 44. A method for forming a stratum consisting of metal particles, comprising the steps of:
 forming an original plurality of discrete metal particles from one of a source of metal material or a precursor for said metal material, said original plurality of discrete metal particles entrained in a gas and thereby forming an aerosol;

15 heating said aerosol to a sufficiently high temperature to densify said particles such that substantially all of said particles include a density substantially as great as a bulk density of said metal material and thereby forming a corresponding plurality of densified discrete metal particles entrained in a gas;

 forming an electrically insulating cover on each of said particles, thereby forming a corresponding plurality of insulator-coated densified discrete metal particles; and

20 depositing said plurality of insulator-coated densified discrete metal particles on a substrate thereby forming a stratum of discrete, electrically isolated metal particles on said substrate.

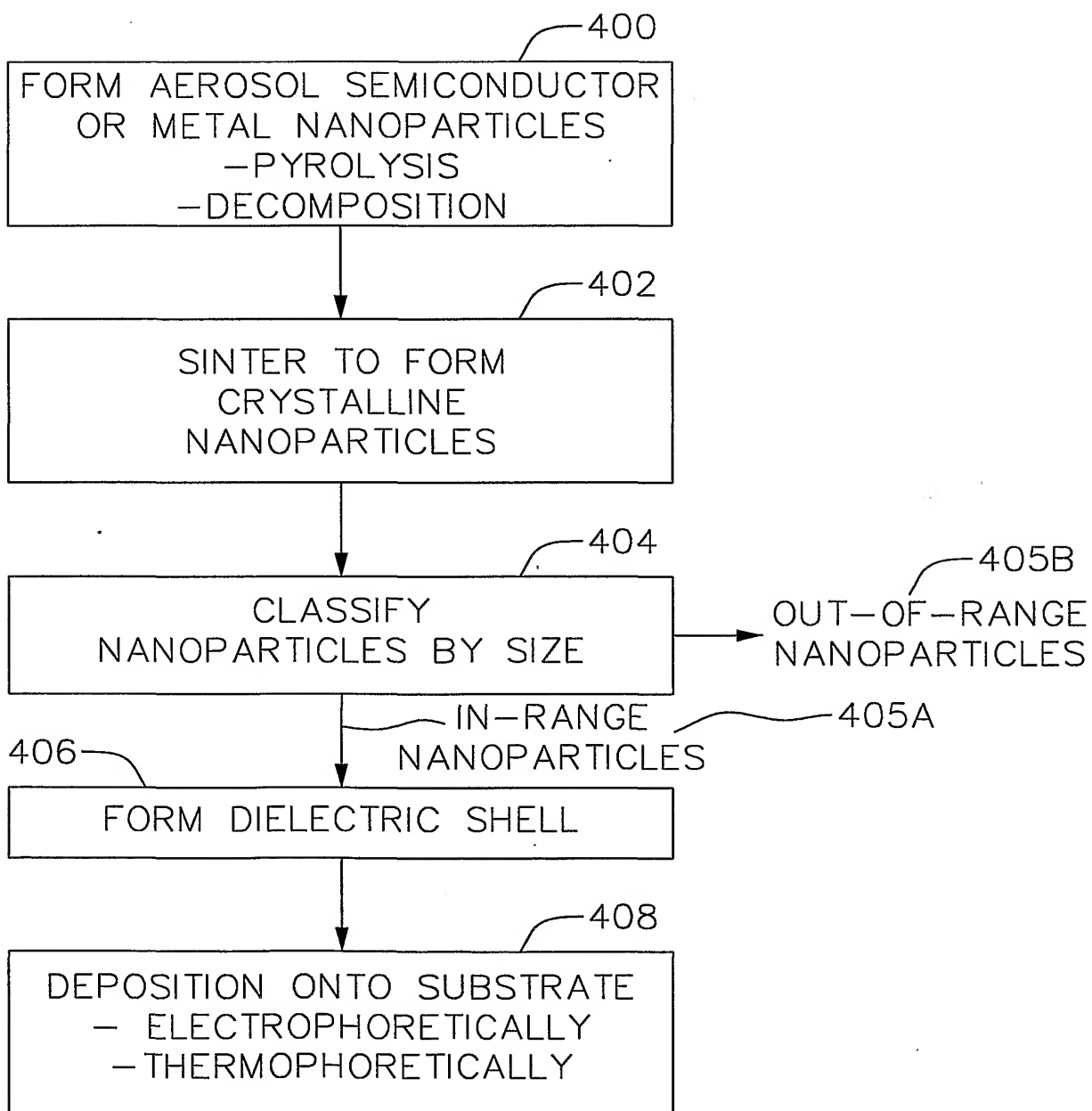
FIG. 1

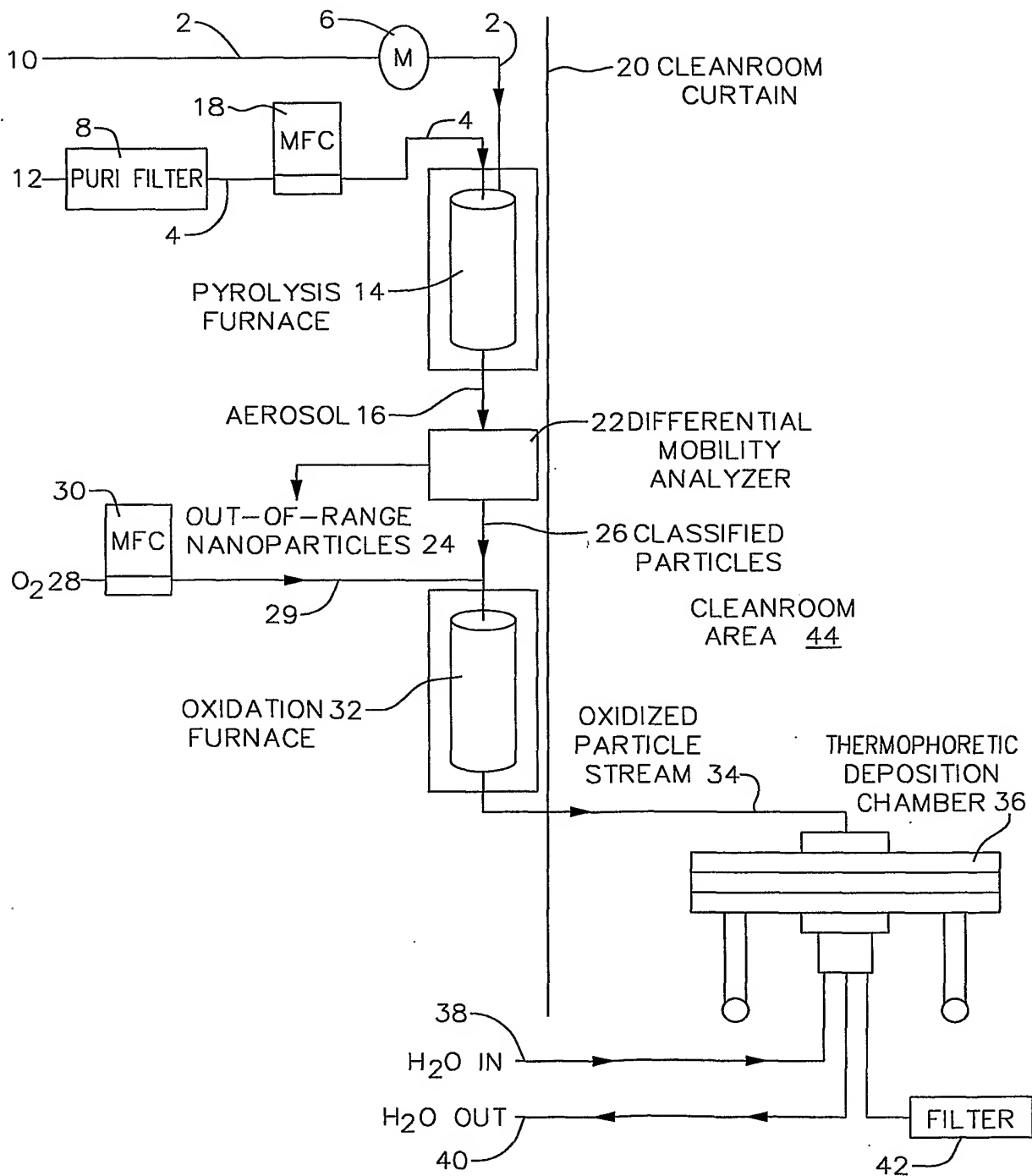
FIG. 2

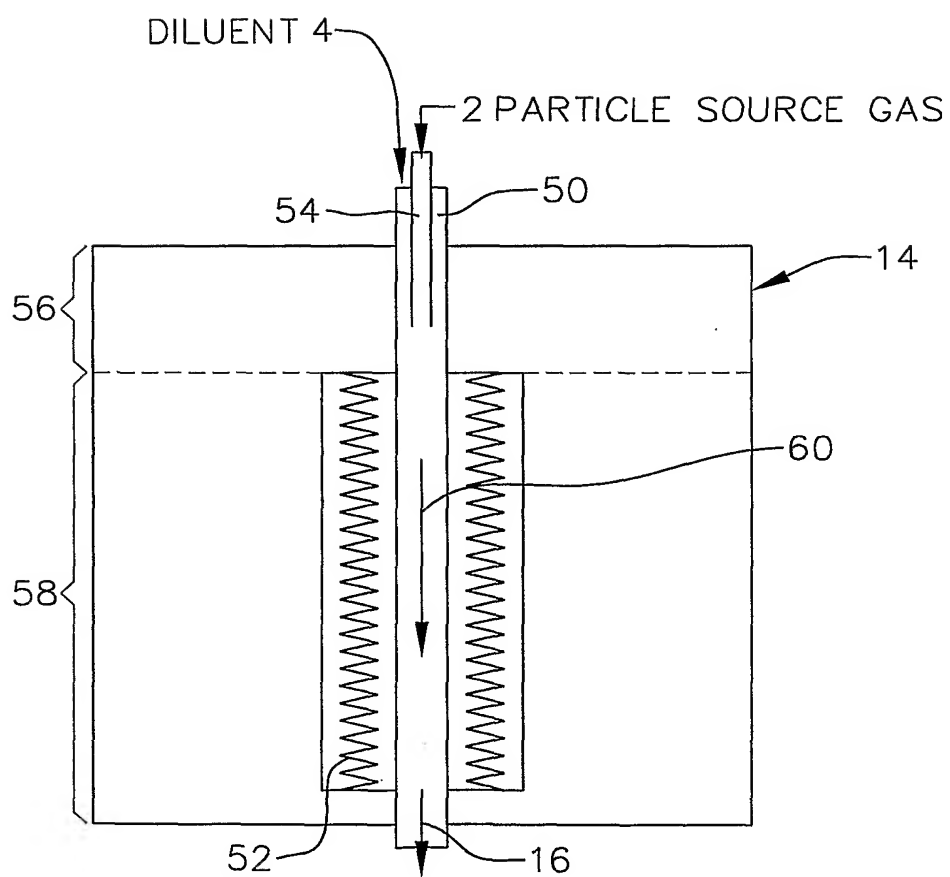
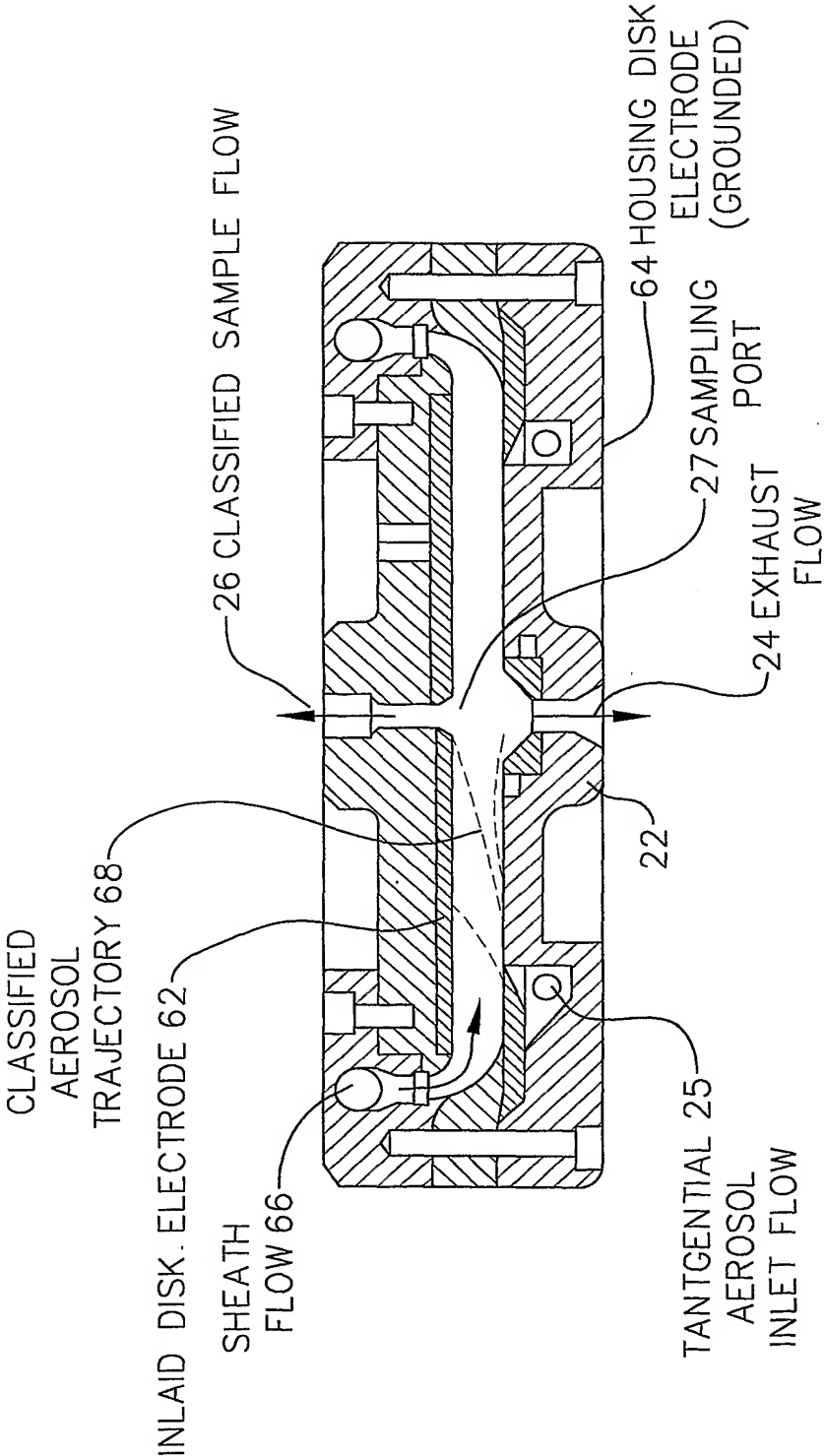
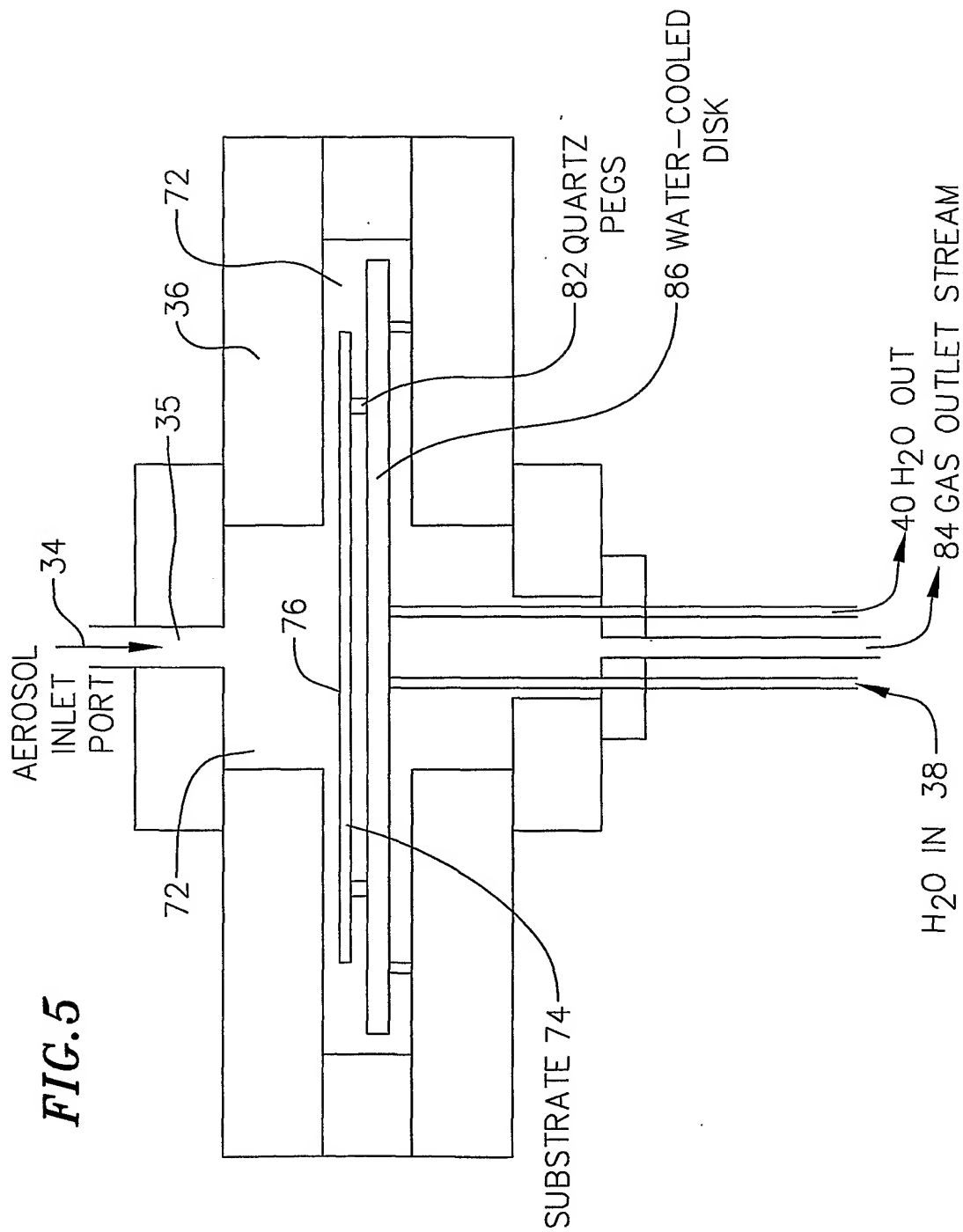
FIG. 3

FIG. 4





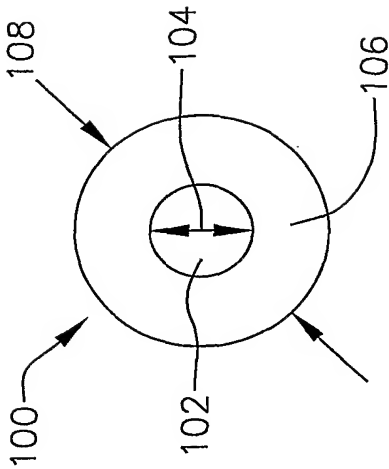


FIG. 6

FIG. 7

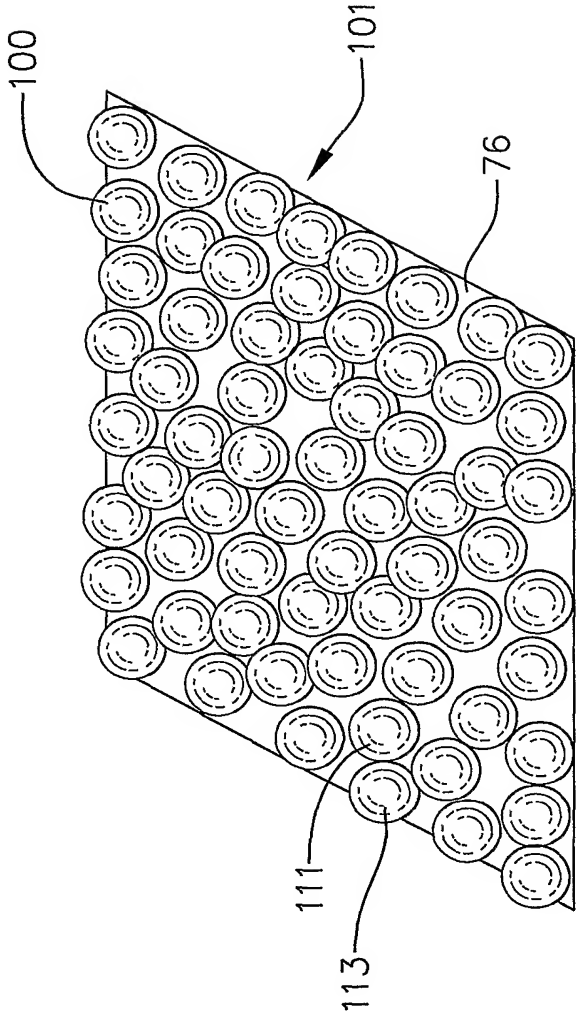


FIG. 8

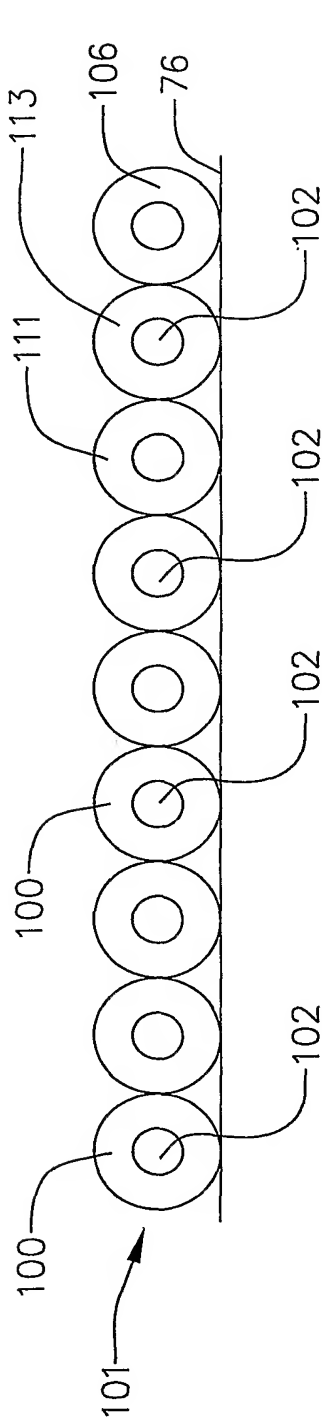


FIG. 9

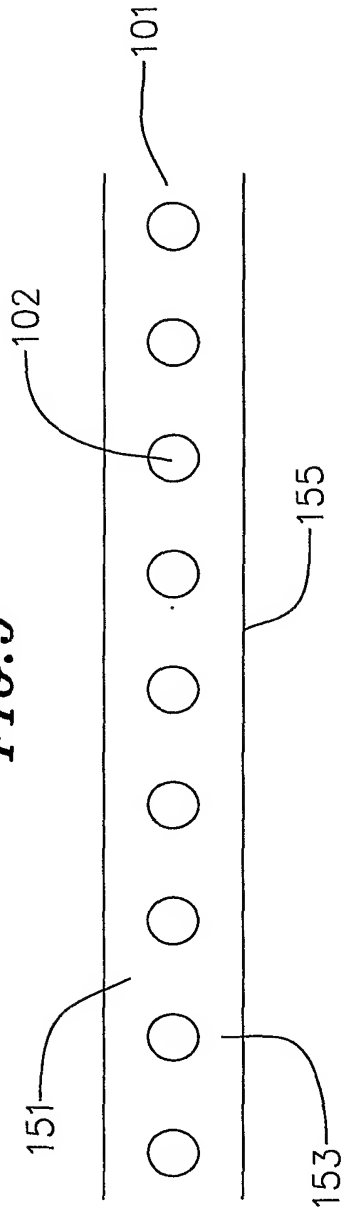


FIG. 10

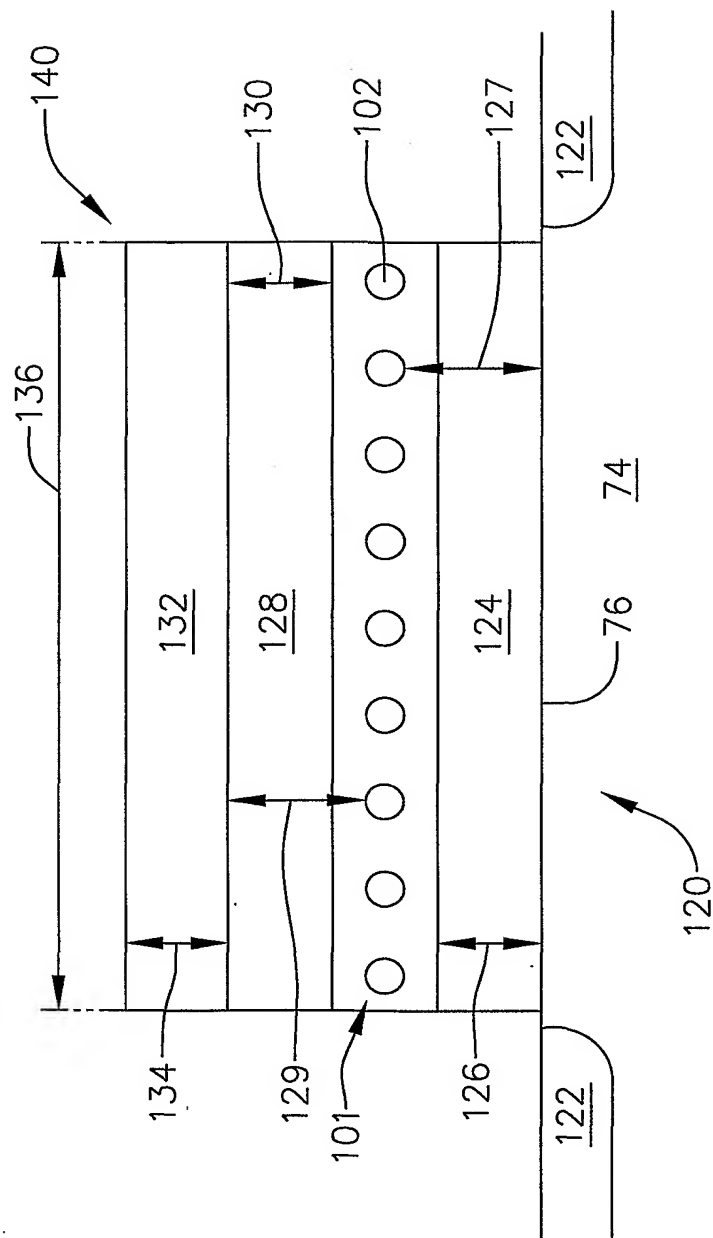


FIG. 12

SUBTHRESHOLD CHARACTERISTICS OF A $0.2\mu\text{m}$
n-TYPE AEROSOL-NANOCRYSTAL FLOATING-GATE
MOSFET(SUBTHRESHOLD SLOPE=200mV/dec;DIBL=100mV/V)

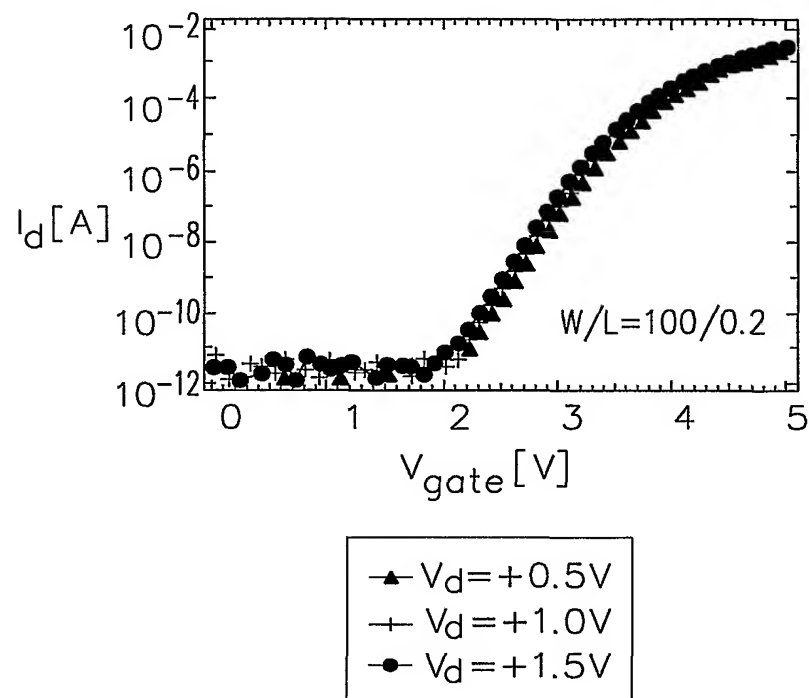


FIG. 13

OUTPUT CHARACTERISTICS OF A $0.2\mu\text{m}$
AEROSOL-NANOCRYSTAL FLOATING-GATE
MOSFET; DRIVE CURRENT= $30\mu\text{A}/\mu\text{m}$

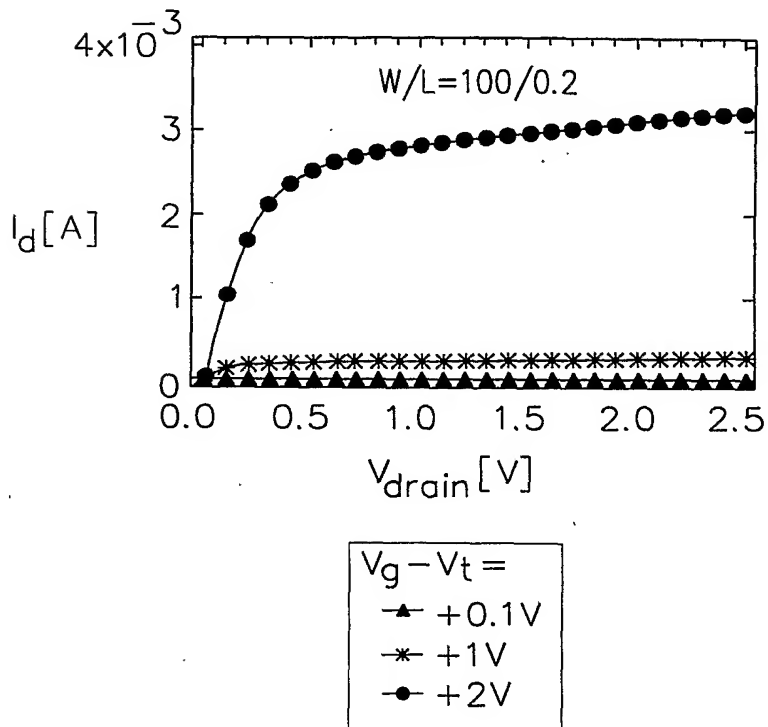


FIG. 14

PROGRAMMING TRANSIENTS (UNIFORM FN TUNNELING)
OF THE NANOCRYSTAL NVM DEVICE

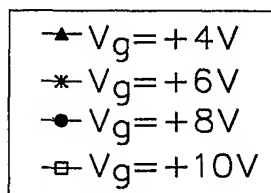
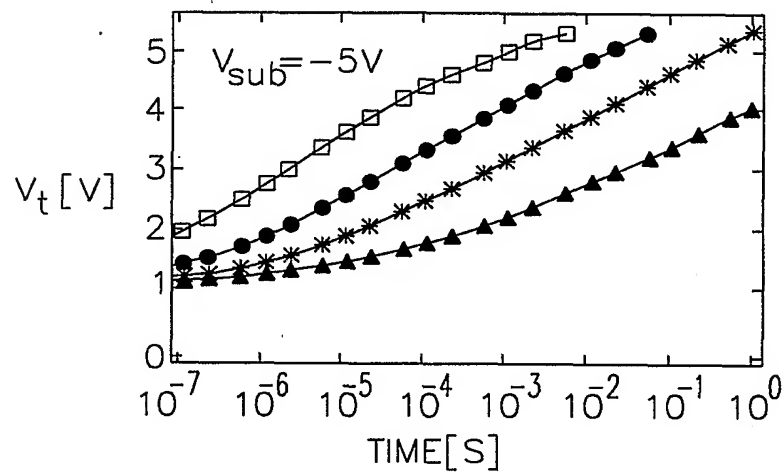


FIG. 15

ERASE TRANSIENTS (UNIFORM FN TUNNELING)

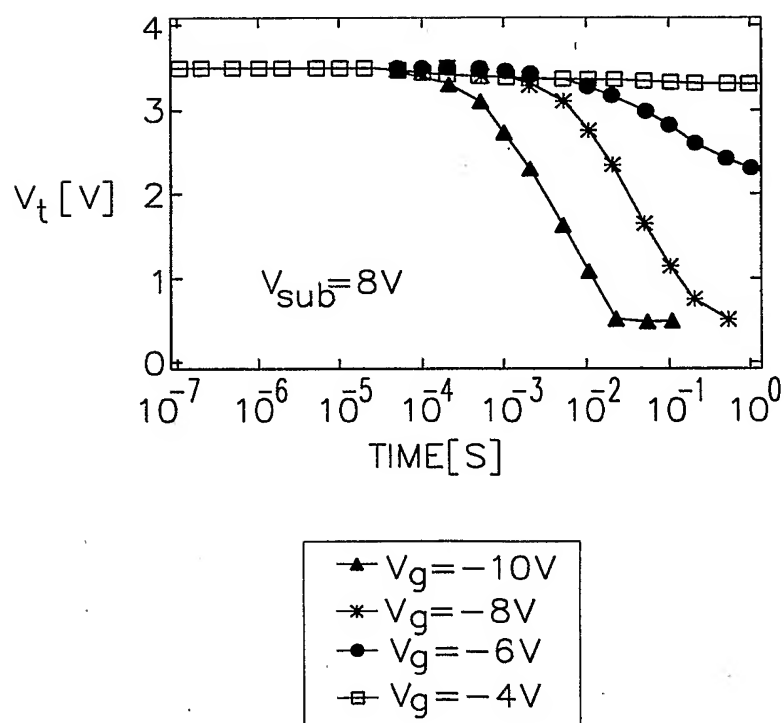
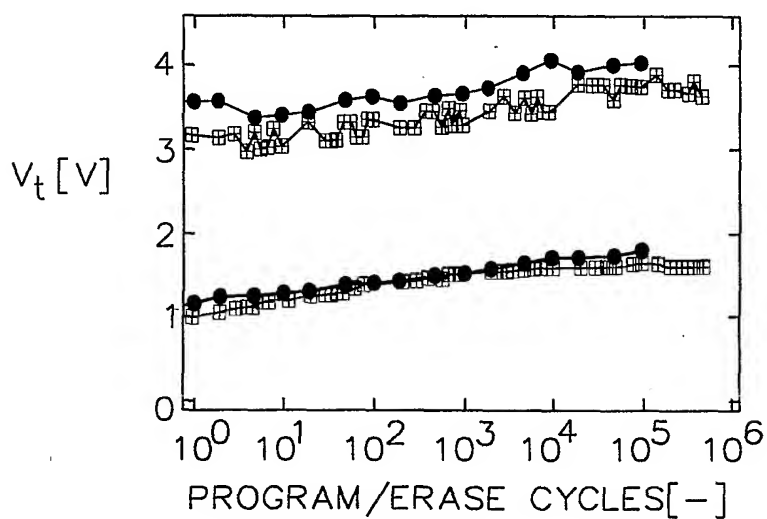


FIG. 16

ENDURANCE CHARACTERISTIC; ONLY LIMITED WINDOW CLOSURE IS OBSERVED AFTER 10^5 PROGRAM/ERASE CYCLES.



P: $V_g = 8V$; $V_{sub} = -5V$; $t_p = 50\mu s$
E: $V_g = -8V$; $V_{sub} = 8V$; $t_E = 100ms$

FIG. 17